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(73)特許権者 000002130

住友電気工業株式会社

大阪府大阪市中央区北浜四丁目5番33号

(72)発明者 岡 良雄

大阪市此花区島屋一丁目1番3号 住友

電気工業株式会社 大阪製作所内

(74)代理人 100064746

弁理士 深見 久郎 (外2名)

審査官 平塚 政宏

最終頁に続く

(54)【発明の名称】 水素発生方法

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(57)【特許請求の範囲】

【請求項1】 陽イオン交換膜の対向する両面に1対の電極を設け、一方に設けられた触媒を含む電極に、メタノールと水を少なくとも含む燃料を接触させ、前記1対の電極に電圧を印加して前記電極から電子を取出すことによって前記電極上で前記メタノールおよび水から水素イオンを発生させる反応を進行させ、発生させた前記水素イオンを、前記陽イオン交換膜の対向する1対の面の他方に設けられた電極において、電子の供給により水素分子に変換することを特徴とする、水素発生方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、電気化学装置を用いた水素発生方法に関する。

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【0002】

【従来の技術】 従来より、炭化水素燃料から水素を発生させるための装置として、リフォーマーがある。

【0003】 リフォーマーにおいて行なわれる水素発生方法には、原料ガスに水蒸気を加えて原料炭化水素を水素、一酸化炭素および二酸化炭素に変換させる水蒸気改質法と、原料炭化水素の一部を燃焼させて水素、一酸化炭素および二酸化炭素を得る部分酸化法(部分燃焼法)とがある。

【0004】 炭化水素を一般にC_nH_mで表わせば、水蒸気改質法において起こる反応を【化1】、部分酸化法において起こる反応を【化2】にそれぞれ示すことができる。

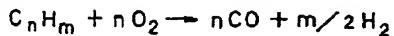
【0005】

【化1】



【0006】

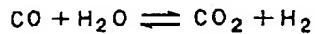
【化2】



【0007】これらの反応において、一酸化炭素の一部は次に示す反応を起こし、これらの反応は平衡を保って進行する。

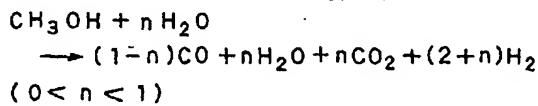
【0008】

【化3】



【0009】

【化4】



【0013】この反応は、0~20kg/cm²の圧力、200~600°Cの温度に設定することが好ましいとされている。

【0014】

【発明が解決しようとする課題】上述した反応を行なった後、リフォーマーを出るガス中には、かなりの濃度の一酸化炭素が含まれている。

【0015】このため、ガス漏れが万一発生した場合、一酸化炭素中毒の危険が伴う。また、リフォーマーを出るガスを触媒反応に用いる際、このガス中に含まれる一酸化炭素が触媒を被毒し、正常な反応を妨げる場合がある。

【0016】そこで、一酸化炭素の残存量を低くするため、【化3】の反応を右に押し進めるべく、一酸化炭素転化器という装置が用いられる。一酸化炭素転化器では、発熱反応である【化3】の反応を押し進めるために、まず350°C~370°C程度に反応温度を設定し、反応速度を高めるため鉄-クロム系などの触媒を用いて、いわゆる高温転化(Hot Shift)を行ない、さらに、銅-亜鉛系の触媒を用いて、200~230°C程度で低温転化(Cold Shift)を行なわせる。これにより一酸化炭素濃度を減少させることができる。

【0017】燃料がアルコールの場合は、この改質反応の後、改質ガスのCOをさらに低減するため、COシフト触媒が用いられる。COシフト処理では、COがH₂Oとの反応により1%程度の濃度にまで低減される。また、さらにCO濃度を引き下げるためには、第2のCO低減装置によって、改質ガスをさらに空気と反応させることにより、100ppmまで低減が可能である。しかし、このような方法では、装置が複雑になり、高温を要

【0010】【化1】は吸熱反応で、他の反応は発熱反応である。したがって、【化1】の反応では外部から加熱する必要があり、通常、ニッケル系の触媒を充填した耐熱金属製の反応管で、温度800°C~900°Cにおいて反応が行なわれる。一方、このような温度では、【化3】および【化4】の反応はあまり右側に進行せず、たとえば850°Cでの反応の場合、二酸化炭素の濃度は10 3~14%、メタンの濃度は3~4%である。

【0011】また、炭化水素の代わりにアルコールの一種であるメタノールを用いた場合は、水と次式のような反応で改質が進行する。

【0012】

【化5】

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【0023】1対の電極は、白金、パラジウム、ロジウム、ルテニウム、金、イリジウムおよびこれらの元素の少なくともいずれかを含む合金等の触媒材料自体から形成してもよいし、導電性のカーボン電極等に触媒材料を担持させたもの等から形成してもよい。

【0024】本発明に従う電極は、たとえば、陽イオン交換膜の膜表面の多孔構造内に、電極材料を析出させることによって形成することができる。その他、本発明に従う電極は、導電性電極基材に触媒材料を電解または無電解メッキすること等により形成することができる。

【0025】本発明に使用する装置において、燃料供給手段は、たとえば、電極の一方に燃料を接触させるため、燃料を収容する容器もしくは槽、該容器もしくは槽に燃料を所定の圧力で送り込むためのポンプ等を備えることができるが、これらに限定されず、電極に燃料を供給する機構であれば、いかなるものも用いることもできる。

【0026】本発明に使用する装置において、燃料には少なくともメタノールおよび水を含むものを用い、一方の電極から水素イオン、他方の電極から水素分子を発生させることができる。このような装置において、電極に含まれる触媒として、白金、パラジウム、ロジウム、ルテニウム、金、イリジウムおよびこれらの元素の少なくともいずれかを含む合金等が好ましく用いられる。

【0027】また、上述した水素を発生させる装置において、他方の電極側に、水素を選択的に透過させることができるとする材料からなる膜を設けることができる。このような膜は、水素透過膜として名づけることができ、水素分子の透過率が、他の物質の透過率に比べて高いものである。このような膜として、たとえば、ポリイミド、ポリスチレン等の高分子からなる膜、Pd合金からなる膜、Ti系、Mm系(Mmはミッシュメタルを示す)、La系、Mg系等の水素吸蔵合金などからなる膜を用いることができる。

【0028】また、上述した装置により水素を発生する方法を提供することができ、この方法は、陽イオン交換膜の対向する両面に1対の電極を設け、一方に設けられた触媒を含む電極に、メタノールと水を少なくとも含む燃料を接触させ、1対の電極に電圧を印加して電極から電子を取り出すことによって電極上でメタノールおよび水から水素イオンを発生させる反応を進行させ、発生させた水素イオンを陽イオン交換膜の対向する1対の面の他方に設けられた電極において、電子の供給により水素分子に変換することを特徴とする。

【0029】

【作用】本発明の作用機構を図を用いて以下に説明する。

【0030】図1は、本発明に従う電気化学装置の一例を示す模式図である。電気化学装置100において、たとえば、固体高分子電解質膜からなる陽イオン交換膜1

01の両側には、白金触媒をそれぞれ担持させた燃料用電極102および対向電極103が設けられる。

【0031】このような陽イオン交換膜と1対の電極からなる接合体は、たとえば、セバレータ106と107の間に挟むことができる。燃料用電極102側のセバレータには、燃料供給用兼CO₂排出用溝108a～eがさらに形成され、対向電極103側のセバレータ107には、水素排出用溝109a～eがさらに形成されている。

【0032】燃料用電極102には、燃料を液体または気体の状態で燃料供給用兼CO₂排出用溝108a～eに通過させることにより、燃料が供給され、かつ電極に接触される。

【0033】燃料用電極102と対向電極103は、セバレータ106および107をそれぞれ介して、外部回路104に電気的に接続される。両電極の間には、電圧が印加され、燃料用電極102側がプラス、対向電極103側がマイナスとされる。

【0034】上述した装置において、燃料用電極102に燃料であるメタノールとともに水または水蒸気を供給し、外部回路104を通じて、燃料用電極102から電子を引き抜くように電圧を印加する。その結果、燃料用電極102では、次の反応が進行する。

【0035】
【化6】CH₃OH + 2H₂O → CO₂ + 6e⁻ + 6H⁺
【0036】このようにして発生した水素イオンは、陽イオン交換膜を通過し、対向電極103で次のように変換される。

【0037】
【化7】6H⁺ + 6e⁻ → 3H₂
【0038】このようなプロセスにより、対向電極103側で、水素を選択的に生成させることができる。したがって、本発明のプロセスによれば、CO₂の生成は抑制される。

【0039】また、対向電極で生じたガスを、上述した水素透過膜を介して採集すれば、水蒸気や他の不純物の濃度を低下させ、純度の高い水素ガスを得ることができる。

【0040】
【実施例】
実施例1

図1に示す装置を用いて水素ガスを製造した。

【0041】本実施例において、電極は次のようにして形成した。固体高分子電解質膜からなる陽イオン交換膜として、NAFION117TM(デュポン社製)を用いた。金属塩として、3%塩化白金酸液、還元剤として1%NaBH₄溶液を用い、陽イオン交換膜に還元剤を浸透させた後、膜表面を塩化白金酸溶液に接触させて、白金層を析出させた。この方法により、膜の両面に、多孔質の白金触媒層を形成し、1対の電極とした。

【0042】このように膜の両側に電極が形成された接合体を組込んだ図1の装置において、燃料用電極102側に、モル比がメタノール：水=1：2のメタノール－水混合液を供給し、接合体からなるセルの温度を30°Cに設定した。そして、燃料用電極102側をプラスとし、燃料用電極102と対向電極103の間に0.2Vの電圧を加えたところ、1.0mA/cm²の電流が流れ、燃料用電極102からCO₂が、対向電極103から水素ガスが発生した。発生した水素中には一酸化炭素は検出されなかった。

【0043】実施例2

実施例1の装置において、対向電極上に水素透過膜としてポリイミド高分子膜を設け、この膜を介して水素を採取した。実施例1と同様な条件にて、燃料用電極と対向電極の間に0.2Vの電圧を印加したところ、1.0mA/cm²の電流が流れ、燃料用電極からCO₂が、対向電極から水素ガスが発生した。ポリイミド高分子膜を介して採取された水素中には、一酸化炭素は検出されなかった。

【0044】

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*【発明の効果】以上説明したように、本発明によれば、従来のような複雑な反応系およびフローシステムは必要でなく、非常にシンプルな装置によって、純度の高い水素を生成させることができる。本発明によれば、CO等の不純物の生成は抑制される。

【0045】このため、一酸化炭素による中毒の危険が回避されるとともに、生成される水素ガスについて、触媒の被毒による化学反応性の低下も防止される。

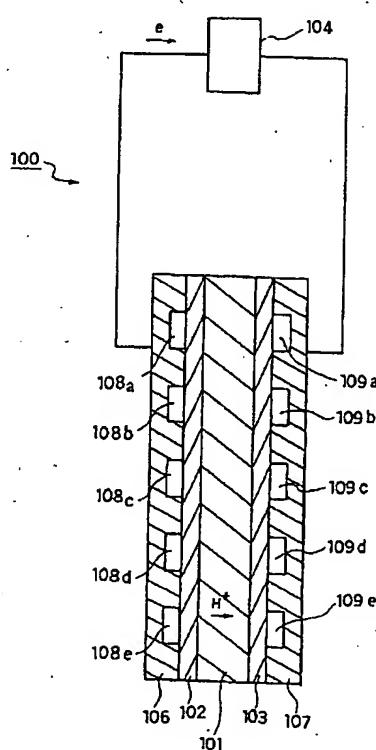
【図面の簡単な説明】

10 【図1】本発明に従う電気化学装置の一具体例を示す概略断面図である。

【符号の説明】

- 100 電気化学装置
- 101 陽イオン交換膜
- 102 燃料用電極
- 103 対向電極
- 104 外部回路
- 106 セバレータ
- 107 セバレータ

【図1】



フロントページの続き

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エネルギー読本, 日本, オーム社, 1982
年 1月25日, 第1版, 149-152,
「[2] 燃料電池の原理」の項

(58)調査した分野(Int.Cl.) , D.B名)

C25B 1/02

C01B 3/32

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3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Industrial Application] This invention relates to the hydrogen generating approach of having used electrochemistry equipment.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the hydrogen generating approach of having used electrochemistry equipment.

[0002]

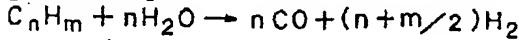
[Description of the Prior Art] Conventionally, there is a reformer as equipment for generating hydrogen from a hydrocarbon fuel.

[0003] There are a steam reforming process which a steam is added [steam reforming process] to material gas and transforms coal-for-coke-making-ized hydrogen to hydrogen, a carbon monoxide, and a carbon dioxide, and the partial oxidation method (partial combustion process) for burning a part of coal-for-coke-making-ized hydrogen and obtaining hydrogen, a carbon monoxide, and a carbon dioxide in the hydrogen generating approach performed in a reformer.

[0004] Generally it is C_nH_m about a hydrocarbon. If expressed, the reaction which occurs the reaction which occurs in a steam reforming process in [-izing 1] and a partial oxidation method can be shown in [-izing 2], respectively.

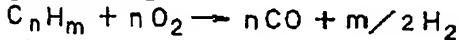
[0005]

[Formula 1]



[0006]

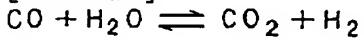
[Formula 2]



[0007] In these reactions, liftings and these reactions maintain a balance for the reaction which shows some carbon monoxides below, and it goes on.

[0008]

[Formula 3]



[0009]

[Formula 4]



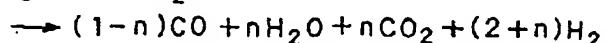
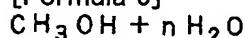
[0010] [-izing 1] is endothermic reaction and other reactions are exothermic reaction. Therefore, it is necessary to heat from the outside and a reaction is usually performed in the temperature of 800 degrees C - 900 degrees C by the coil of heat-resistant metal filled up with the catalyst of a nickel system at the reaction of [-izing 1]. On the other hand at such temperature, the reaction of [-izing 3] and [-izing 4] seldom advances on right-hand side, for example, in the case of a 850-degree C

reaction, the concentration of methane of the concentration of a carbon dioxide is 3 - 4% 13 to 14%.

[0011] Moreover, when the methanol which is a kind of alcohol instead of a hydrocarbon is used, reforming advances at a reaction like water and a degree type.

[0012]

[Formula 5]



$$(0 < n < 1)$$

[0013] This reaction is 0-20kg/cm². It is made desirable to set it as a pressure and the temperature of 200-600 degrees C.

[0014]

[Problem(s) to be Solved by the Invention] After performing the reaction mentioned above, the carbon monoxide of remarkable concentration is contained in the gas which comes out of a reformer.

[0015] For this reason, if gas leakage should occur, the risk of carbon monoxide poisoning follows. Moreover, in case the gas which comes out of a reformer is used for catalytic reaction, the carbon monoxide contained in this gas may carry out poisoning of the catalyst, and may bar a normal reaction.

[0016] Then, equipment called a carbon monoxide converter is used in order to make the amount of survival of a carbon monoxide low, and to push the reaction of [-izing 3] on the right. In order to push the reaction of the [-izing 3] which is exothermic reaction, reaction temperature is first set as 350 degrees C - about 370 degrees C, in order to raise a reaction rate, the so-called elevated-temperature inversion (Hot Shift) is performed using catalysts, such as an iron-chrome system, and low-temperature inversion (Cold Shift) is made to perform at about 200-230 degrees C further with a carbon monoxide converter using the catalyst of a copper-zinc system. Thereby, carbon monoxide concentration can be decreased.

[0017] When a fuel is alcohol, in order to reduce CO of reformed gas further, CO shift catalyst is used after this reforming reaction. In CO shift processing, CO is reduced by even about 1% of concentration by the reaction with H₂O. Furthermore, in order to reduce CO concentration, it can decrease to 100 ppm by making reformed gas react with air further with 2nd CO reduction equipment. However, by such approach, equipment becomes complicated and there is a problem of requiring an elevated temperature etc.

[0018] The purpose of this invention is to offer the approach of generating hydrogen gas from a fuel, without generating most carbon monoxides not using the above complicated flow systems.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] After performing the reaction mentioned above, the carbon monoxide of remarkable concentration is contained in the gas which comes out of a reformer.

[0015] For this reason, if gas leakage should occur, the risk of carbon monoxide poisoning follows. Moreover, in case the gas which comes out of a reformer is used for catalytic reaction, the carbon monoxide contained in this gas may carry out poisoning of the catalyst, and may bar a normal reaction.

[0016] Then, equipment called a carbon monoxide converter is used in order to make the amount of survival of a carbon monoxide low, and to push the reaction of [-izing 3] on the right. In order to push the reaction of the [-izing 3] which is exothermic reaction, reaction temperature is first set as 350 degrees C – about 370 degrees C, in order to raise a reaction rate, the so-called elevated-temperature inversion (Hot Shift) is performed using catalysts, such as an iron-chrome system, and low-temperature inversion (Cold Shift) is made to perform at about 200–230 degrees C further with a carbon monoxide converter using the catalyst of a copper-zinc system. Thereby, carbon monoxide concentration can be decreased.

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[0018] The purpose of this invention is to offer the approach of generating hydrogen gas from a fuel, without generating most carbon monoxides not using the above complicated flow systems.

[0019] The further purpose of this invention is from the fuel containing a methanol and water to offer the approach of generating hydrogen, without generating most carbon monoxides electrochemically.

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MEANS

[Means for Solving the Problem] The electrochemistry equipment used for this invention is formed in one pair of front faces on which the cation exchange membrane which has one pair of front faces which counter, and cation exchange membrane counter, respectively, and is equipped with the fuel-supply means for supplying a fuel to one side of one pair of electrodes which consist of ingredients including a catalyst, and one pair of electrodes. With the electrochemistry equipment used for this invention, the cation which is made to generate a cation and by which while a fuel is supplied was generated from the fuel in the electrode is transformed to a molecule by electronic supply on one pair of another side of an electrode through cation exchange membrane.

[0021] In this invention, cation exchange membrane will not be limited, especially if a cation is made to penetrate alternatively. As cation exchange membrane, the solid-state polyelectrolyte film, the film which consists of a matrix containing a phosphoric acid, the film which consists of a matrix containing a sulfuric acid, the film which consists of a solid electrolyte can be mentioned. Moreover, the ion exchange membrane which has a sulfonic acid, phosphonic acid, a sulfate, phosphoric ester, etc. can be used as a cation-exchange radical.

[0022] In this invention, the alloy of platinum, palladium, a rhodium, a ruthenium, gold, iridium, and these elements which contains either at least can be used for the catalyst contained in an electrode.

[0023] One pair of electrodes may be formed from the catalyst ingredient itself, such as an alloy of platinum, palladium, a rhodium, a ruthenium, gold, iridium, and these elements which contains either at least, and may be formed from the thing which made the conductive carbon electrode etc. support a catalyst ingredient.

[0024] The electrode according to this invention can be formed by depositing an electrode material in the porous structure on the front face of the film of cation exchange membrane. In addition, the electrode according to this invention can form a catalyst ingredient in a conductive electrode substrate electrolysis, by carrying out electroless deposition, etc.

[0025] In the equipment used for this invention, since a fuel is contacted to one side of an electrode, it can have a pump for sending a fuel into the container or tub which holds a fuel, this container, or a tub by the predetermined pressure etc., but a fuel-supply means is not limited to these, but if it is a device which supplies a fuel to an electrode, what kind of thing can also be used for it.

[0026] A fuel can be made to generate a hydrogen ion and the electrode of another side to a hydrogen content child from one electrode in the equipment used for this invention using what contains a methanol and water at least. In such equipment, the alloy of platinum, palladium, a rhodium, a ruthenium, gold, iridium, and these elements which contains either at least is preferably used as a catalyst included in an electrode.

[0027] Moreover, in the equipment made to generate the hydrogen mentioned above, the film which consists of an ingredient which can make hydrogen penetrate alternatively to the electrode side of

another side can be prepared. Such film can be named as a hydrogen permeable film, and its permeability of a hydrogen content child is high compared with the permeability of other matter. The film which consists of hydrogen storing metal alloys, such as the film which consists of macromolecules, such as polyimide and polystyrene, film which consists of a Pd alloy, Ti system, Mm system (Mm shows a misch metal), La system, and Mg system, etc. as such film can be used.

[0028] The approach of generating hydrogen with the equipment mentioned above can be offered. Moreover, this approach To an electrode including the catalyst which prepared one pair of electrodes in both sides to which cation exchange membrane counters, and was prepared in one side The reaction which generates a hydrogen ion is advanced from a methanol and water on an electrode by contacting the fuel which contains a methanol and water at least, impressing an electrical potential difference to one pair of electrodes, and picking out an electron from an electrode..It is characterized by changing the generated hydrogen ion into a hydrogen content child by electronic supply in the electrode prepared in another side of one pair of fields where cation exchange membrane counters.

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OPERATION

[Function] The mechanism of action of this invention is explained below using drawing.

[0030] Drawing 1 is the mimetic diagram showing an example of electrochemistry equipment according to this invention. In electrochemistry equipment 100, the electrode 102 for fuels and counterelectrode 103 which made the platinum catalyst support, respectively are prepared in the both sides of the cation exchange membrane 101 which consists of solid-state polyelectrolyte film.

[0031] The zygote which consists of such cation exchange membrane and one pair of electrodes can be inserted among separators 106 and 107. In the separator by the side of the electrode 102 for fuels, it is -cum- CO₂ for fuel supply. Slot 108 a-e for discharge is formed further, and slot 109 a-e for hydrogen discharge is further formed in the separator 107 by the side of a counterelectrode 103.

[0032] In the electrode 102 for fuels, it is -cum- CO₂ for fuel supply in the condition of a liquid or a gas about a fuel. By passing slot 108 a-e for discharge, a fuel is supplied and it is contacted by the electrode.

[0033] The electrode 102 for fuels and a counterelectrode 103 are electrically connected to an external circuit 104 respectively through separators 106 and 107. Between two electrodes, an electrical potential difference is impressed and a plus and counterelectrode 103 side is considered for the electrode 102 side for fuels as minus.

[0034] In the equipment mentioned above, water or a steam is supplied to the electrode 102 for fuels with the methanol which is a fuel, and through an external circuit 104, an electrical potential difference is impressed so that an electron may be drawn out from the electrode 102 for fuels. Consequently, the next reaction advances in the electrode 102 for fuels.

[0035]

[Formula 6] CH₃OH+2H₂O→CO₂+6e⁻+6H⁺[0036] Thus, the generated hydrogen ion passes cation exchange membrane, and is changed as follows with a counterelectrode 103.

[0037]

[Formula 7] 6H⁺+6e⁻→3H₂[0038] Such a process can be made to generate hydrogen alternatively by the counterelectrode 103 side. Therefore, according to the process of this invention, generation of CO is controlled.

[0039] Moreover, if the gas produced with the counterelectrode is collected through the hydrogen permeable film mentioned above, the concentration of a steam or other impurities can be reduced and hydrogen gas with high purity can be obtained.

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EXAMPLE

[Example]

Hydrogen gas was manufactured using the equipment shown in example 1 drawing 1.

[0041] In this example, the electrode was formed as follows. NAFION117R (Du Pont make) was used as a cation exchange membrane which consists of solid-state polyelectrolyte film. As a metal salt, it is 1%NaBH4 as 3% chloroplatinic acid liquid and a reducing agent. After making a reducing agent permeate cation exchange membrane using a solution, the film front face was contacted in the chloroplatinic acid solution, and the platinum layer was deposited. By this approach, the porous platinum catalyst layer was formed in membranous both sides, and it considered as one pair of electrodes.

[0042] Thus, in the equipment of drawing 1 incorporating the zygote with which the electrode was formed in membranous both sides, the mole ratio supplied the methanol-water mixed liquor of methanol:water =1:2, and set the temperature of the cel which consists of a zygote as 30 degrees C at the electrode 102 side for fuels. And when the electrode 102 side for fuels was considered as plus and the electrical potential difference of 0.2V was applied between the electrode 102 for fuels, and the counterelectrode 103, it is 1.0 mA/cm². A current flows and it is CO₂ from the electrode 102 for fuels. Hydrogen gas was generated from the counterelectrode 103. The carbon monoxide was not detected in the generated hydrogen.

[0043] In the equipment of example 2 example 1, the polyimide poly membrane was prepared as a hydrogen permeable film on the counterelectrode, and hydrogen was collected through this film. When the electrical potential difference of 0.2V was impressed between the electrode for fuels, and the counterelectrode on the same conditions as an example 1, it is 1.0 mA/cm². A current flows and it is CO₂ from the electrode for fuels. Hydrogen gas was generated from the counterelectrode. The carbon monoxide was not detected in the hydrogen collected through the polyimide poly membrane.

[0044]

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the complicated system of reaction and the complicated flow system like before cannot be required, and can make very simple equipment generate hydrogen with high purity, as explained above. According to this invention, generation of impurities, such as CO, is controlled.

[0045] For this reason, while the risk of the poisoning of carbon mono oxide is avoided, the fall of the chemical reactivity by poisoning of a catalyst is also prevented about the hydrogen gas generated.

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CLAIMS

(57) [Claim(s)]

[Claim 1] To an electrode including the catalyst which prepared one pair of electrodes in both sides to which cation exchange membrane counters, and was prepared in one side The reaction which generates a hydrogen ion is advanced from said methanol and water on said electrode by contacting the fuel which contains a methanol and water at least, impressing an electrical potential difference to said one pair of electrodes, and picking out an electron from said electrode. The hydrogen generating approach characterized by changing said generated hydrogen ion into a hydrogen content child by electronic supply in the electrode prepared in another side of one pair of fields where said cation exchange membrane counters.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline sectional view showing one example of electrochemistry equipment of following this invention.

[Description of Notations]

100 Electrochemistry Equipment

101 Cation Exchange Membrane

102 Electrode for Fuels

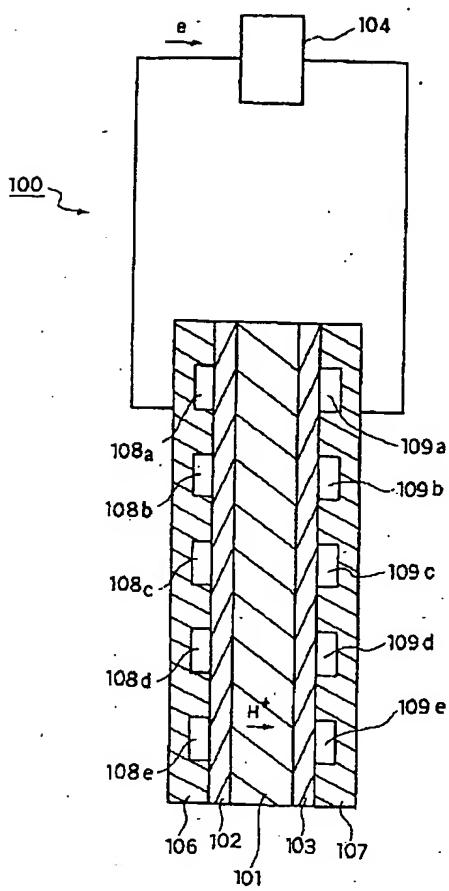
103 Counterelectrode

104 External Circuit

106 Separator

107 Separator

[Translation done.]

Drawing selection drawing 1 

[Translation done.]